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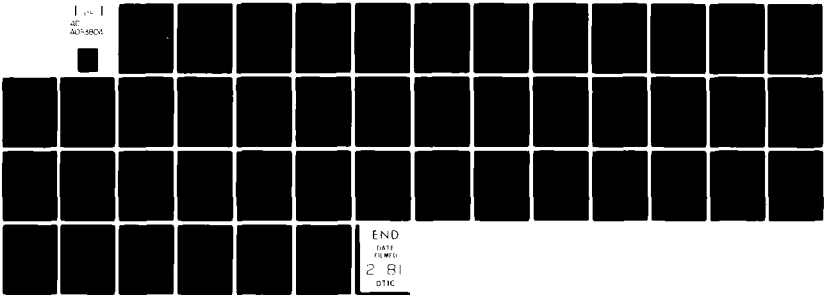

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A procedure for determining the allowed local site symmetry groups, S, for surface adsorbed molecules is presented. An analogy can be drawn between the perturbing field experienced by a matrix isolated molecule in a three-dimensional crystal and that experienced by a molecule adsorbed on a surface. In the former case, the field has the symmetry of the host lattice site whereas in the latter case, the field has the symmetry of the adsite. If the surface is viewed as a homogeneous two-dimensional plane, then the symmetry

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20. Abstract (continued)

of the adsite is described by the group G = $C_{\infty v}$. If the surface cannot be viewed as an unstructured homogeneous plane so that the perturbing field experienced by the adsorbed molecule must be considered on a microscopic level, then the adsite symmetry will be described by the group appropriate for the substrate atoms. This can only be one of the groups G = C_n or G = C_{nv}. The symmetry operations of the local site symmetry group, S, consist of an operation in the molecular point group, M, applied to the molecule combined with an operation in G applied to the substrate. A mapping of the operations in M and G to operations in their isomorphous Longuet-Higgins groups allows the operations to be identified as permutation, P, or permutation-inversion, P*, operations. The operations in M with P operations in G and of P* operations in M with P* operations in G. An adsorbed molecule having M = D_{3h} symmetry is used as an example to demonstrate the procedure for determining S. The local site symmetry group of the adsorbed molecule is, in general, different for the homogeneous surface approximation as opposed to the microscopic surface approximation. An attempt is made to apply predicted spectroscopic selection rules to adsorbed pyridine and ethylene. Several factors which complicate the interpretation of Raman spectra of molecules adsorbed on metal surfaces are discussed, one of these being depolarization effects due to rough surfaces.

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Site Symmetry of Surface Adsorbed Molecules

by

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ABSTRACT

A procedure for determining the allowed local site symmetry groups, S, for surface adsorbed molecules is presented. An analogy can be drawn between the perturbing field experienced by a matrix isolated molecule in a three-dimensional crystal and that experienced by a molecule adsorbed on a surface. In the former case, the field has the symmetry of the host lattice site whereas in the latter case, the field has the symmetry of the adsite. If the surface is viewed as a homogeneous two-dimensional plane, then the symmetry of the adsite is described by the group $G = C_{\infty v}$. If the surface cannot be viewed as an unstructured homogeneous plane so that the perturbing field experienced by the adsorbed molecule must be considered on a microscopic level, then the adsite symmetry will be described by the group appropriate for the substrate atoms. This can only be one of the groups $G = C_n$ or $G = C_{nv}$. The symmetry operations of the local site symmetry group, S, consist of an operation in the molecular point group, M, applied to the molecule combined with an operation in G applied to the substrate. A mapping of the operations in M and G to operations in their isomorphous

Longuet-Higgins groups allows the operations to be identified as permutation, P, or permutation-inversion, P*, operations. The operations in S are restricted to be combinations of P operations in M with P operations in G and of P* operations in M with P* operations in G. An adsorbed molecule having $M = D_{3h}$ symmetry is used as an example to demonstrate the procedure for determining S. The local site symmetry group of the adsorbed molecule is, in general, different for the homogeneous surface approximation as opposed to the microscopic surface approximation. An attempt is made to apply predicted spectroscopic selection rules to adsorbed pyridine and ethylene. Several factors which complicate the interpretation of Raman spectra of molecules adsorbed on metal surfaces are discussed, one of these being depolarization effects due to rough surfaces.

I. Introduction

Since the pioneering work of Fleischmann and co-workers,[1] Raman spectroscopy has been used in numerous investigations of molecules adsorbed on metal surfaces.[2-10] Albrecht and Creighton pointed out that the Raman scattering intensity for pyridine adsorbed on silver surfaces was 10^5- 10^6 times greater than that expected when the number of adsorbed molecules and the normal Raman scattering cross section for pyridine are considered.[11] This conclusion was also arrived at independently by Jeanmaire and Van Duyne.[6] Blondeau and co-workers used radiochemical techniques to establish coverage and determined that the amount of pyridine adsorbed on a silver electrode was 10 - 100 monolayers.[12] This indicates that part of the Raman scattering intensity observed with pyridine adsorbed on silver arises from a greater number of adsorbed molecules as compared to monolayer coverages. The intensity of the pyridine Raman signal may not, therefore, be due entirely to surface enhanced Raman scattering (SERS). An intensity enhancement of $\sim 10^6$, however, has been established by Bergman and co-workers for CN^- adsorbed on silver.[3] Radiochemical methods were also used by these authors to determine that the amount of adsorbed CN^- was on the order of a monolayer.

Smardzewski and co-workers studied the pyridine/silver system in ultrahigh vacuum.[8] A layer of pyridine or deuteropyridine over its previously depositied analog did not show SERS, leading to the conclusion that SERS is only exhibited by those molecules immediately adjacent to the metal surface. These authors did not, however, have

methods available to characterize the surface or to determine pyridine coverage. A similar study by Zwemer et al. shows that SERS is important beyond the first layer of adsorbed molecules.[13] Pyridine film thicknesses were monitored by Auger electron spectroscopy. The distance of a pyridine or deuteropyridine layer to the silver surface was controlled by first depositing a known thickness of its analog. The Raman signal contributed by the tenth monolayer was shown to be approximately 10% that of the first monolayer. Raman scattering from molecules 50 Å away from the surface could be detected. This apparent contradiction between the results of Smardzewski et al. and those of Zwemer et al. can be explained with the assumption that many layers of pyridine, or deuteropyridine, were being deposited in the experiments by Smardzewski and co-workers rather than monolayer coverages.

In order to observe SERS, it is apparently necessary for the surface to be initially roughened. This is usually accomplished by electrochemical cycling,[1,9-11,14,15] although other methods have also been used successfully to roughen the metal surface. Bergman and co-workers have shown that electrochemical cycling is not necessary during electrochemical roughening.[3] Their procedure is to apply a positive potential of approximately 0.5 V (relative to SCE) to the silver electrode in aqueous alkali fluoride, followed by removal of the electrode from solution while still under potentiostatic control. Moskovits and DiLella used vapor deposited silver without additional roughening in a Raman study of adsorbed ethylene and propylene.[16] This procedure has also been used by Glass and co-workers for preparing silver surfaces.[17] Sennett and Scott have shown that silver

surfaces deposited by this method consist of small particles whose size depends upon the evaporation conditions.[18] Rowe and co-workers[19] and Zwemer et al.[13] used a photochemical etching procedure in which I_2 is first deposited, followed by laser excitation at 4880 Å. Ion sputtering [8,20] and mechanical polishing[21] are other methods which have been used to roughen metal surfaces.

Although some roughening of the metal surface is required to observe SERS, Raman scattering intensities have been found to decrease with excessive roughening.[6,9] Electrochemically reformed silver surfaces have been characterized by Evans and co-workers using scanning electron microscopy, Auger electron spectroscopy, and secondary ion mass spectroscopy.[22] The reformed silver surface was found to be quite pure, except for a layer of adsorbed Cℓ originally present as the electrolytic solute. The adsorbed Cℓ could be removed by ion sputtering which indicates that it is only a surface contaminate. Scanning electron micrographs showed that the reformed silver surface consisted of a nodular deposit.

Various models have been proposed to account for the observed enhancement of Raman scattering intensitites found with surface adsorbed molecules. King and co-workers suggested that SERS results from the image field arising from the metal surface.[23] Intensity enhancements of 10^5 - 10^6 are predicted by their classical electrostatic model. Surface roughening, however, does not enter into the model. A similar model has been advanced by Efrima and Metiu.[24-26] According to their model, the predicted intensity enhancement arises from a) a primary electric field at the molecule due to the incident light, b) a secondary electric field due to reflection of light from the surface, and c) reflection by the surface of scattered light

to the detector. Raman scattering intensities for molecules adsorbed on metal surfaces are predicted to be as much as 10^6 greater than for unadsorbed molecules. The experimental requirement that the surface be roughened is not accounted for.

Hexter and Albrecht have suggested that surface plasmons may be responsible for SERS.[27] A mixing of the molecular electronic states of the adsorbed molecule with the surface plasmons of the metal substrate provides a continuum of excited states for Raman scattering. The frequency distribution of these states may have a peak at a frequency other than that of the surface plasmon frequency. According to Philpott, this can result in resonance Raman, or preresonance Raman, scattering at frequencies which in the absence of a metal substrate would yield only normal Raman scattering.[28] The role of surface roughness in this model is to enable coupling of the incident photons to the otherwise non-radiative surface plasmons.

Jeanmaire and Van Duyne proposed that SERS is caused by strong electric fields in the electric double layer adjacent to the surface in solutions.[6] Later experiments, however, discount this idea. Otto,[21] as well as Bergman et al.,[3] have observed SERS from adsorbed molecules after the electrode is removed from solution and dried. SERS has also been found when ultrahigh vacuum techniques are used, which indicates that the electric double layer in solution experiments is of minor importance.[8,13,19]

A more recent model has been proposed by McCall and co-workers to explain SERS.[20] As a model system, these authors chose a molecule adsorbed on a plasma sphere with radius much smaller than the wavelength of light. This sphere will then amplify the electric field due to incident light, and also amplify the electric field

of Raman scattered light. Raman scattering enhancements of 10^4 - 10^5 are predicted by this model. Similar ideas have been used in a model by Wang et al.[29] In these models, the enhancement is a result of extraordinarily large local fields in the vicinity of metallic spheres of small diameter. A roughened surface is then imagined to be a collection of such spheres.

An important advantage of infrared and Raman spectroscopy of surface adsorbed molecules is that molecular, rather than elemental, information is obtained from the spectroscopy. In some instances, knowledge of the vibrational selection rules should allow the orientation of the adsorbed molecule to be determined.

According to classical image theory, a charge adsorbed at a distance d above the surface of a perfect electrical conductor will induce an image charge in the conductor at a distance d below the surface.[30] Pearce and Sheppard have suggested that a metal surface selection rule is operative for molecules adsorbed on metal surfaces, its basis being that incident light interacts with the adsorbed molecule-image molecule system, not just the adsorbed molecule.[31] Physical arguments were used to demonstrate that only those molecular vibrations having non-zero dipole moment derivative components perpendicular to the surface would be infrared active. They applied this to explain the infrared spectra of ethylene adsorbed on silica-supported metal catalysts. These ideas were further advanced by Hexter and Albrecht, who used group theory to predict the infrared and Raman activity of molecules adsorbed on metal surfaces.[27] The adsorbed and image molecules were shown to be related by the symmetry operation, R, which is a mirror reflection through the plane of the surface combined with charge conjugation.

Nichols and Hexter extended the group theory arguments using the properties of Shubnikov Type II, or grey, groups.[32]

In the preceding treatments, an effective surface site symmetry, S, was assumed for the adsorbed molecule. A detailed determination of allowed surface site symmetries was not considered. The procedure for determining S from the free molecule point group, M, and the adsite symmetry, G, appropriate for the surface substrate atoms is presented in Section II. Two views of the surface are considered. In the "homogeneous" surface approximation, the surface is treated as a smooth unstructured plane whereas for a "microscopic" surface, the surface substrate atoms have a particular factor group.

Examples are given in Section III for the application of the group theory presented in Section II. A molecule having D_{3h} symmetry adsorbed on a surface is used as a model system. Two orientations of the adsorbed molecule are considered.

The determination of the orientation of adsorbed molecules is complicated by factors other than the group theoretical selection rules, one of these being depolarization effects due to rough surfaces. In Section IV, several difficulties with Raman spectral analysis of adsorbed molecules are discussed.

In Section V, an attempt is made to determine the orientations of adsorbed pyridine and ethylene on silver using the results of existing Raman studies.

II. Group Theory

In this section, a procedure for determining the local site symmetry, S, of an adsorbed molecule is presented. The group S is obtained from the point group of the free molecule, M, and the point group, G, appropriate for the adsite. The effects of image molecules induced in the substrate are accounted for by the correlation of the group S to the group $\bar{S}$, which is the point group of the system, molecule-plus-image. Factor group effects are also briefly considered.

A. Local Site Symmetry

The "effective" local site symmetry, S, of the adsorbed molecule may be derived in the manner used by Miller and Decius for matrix isolated molecules in three-dimensional crystals.[33] Those authors used the methods of group theory developed by Longuet-Higgins. Longuet-Higgins describes the symmetry of a system in terms of permutations of identical particles and inversion of particle positions through the center of mass.[34] A particular permutation can be written as

$$P(r) = Q(r_e + T\rho)$$

where ρ is an internal coordinate, T is an operation of the point group, r_e is a position vector describing the equilibrium positions of the atoms, Q is a rotation, and $r = r_e + \rho$. The permutation-inversion operations, P*, are given by P* = PE*, where E* is an inversion of all particles through the center of mass. All the operations of a point group can be mapped into P and P* operations.

Following Miller and Decius,[33] the symmetry elements of the free molecule, M, and the group G, describing the symmetry of the host site, or adsite, may each be divided into two sets consisting of permutation operations, P, and permutation-inversion operations, P*. The elements of the group describing the surface isolated molecule are products of P operations in M with P operations in G and P* operations in M with P* operations in G. The point group appropriate for the situation in which the molecule is allowed to rotate at the site is given by

$$S_r = M(P) \otimes G(P) + M(P^*) \otimes G(P^*)$$

where M(P) and G(P) are the subsets of P operations in M and G, respectively, and M(P*) and G(P*) are the respective subsets of P* operations. The group, S_h, appropriate for the high barrier limit will be a subgroup of S_r and, in addition, a common subgroup of M and G. The problem of determining S_r and S_h is then that of identifying the P and P* elements of M and G.

B. Adsite Symmetry

A surface may be viewed in two ways. It may be considered to be a two-dimensional homogeneous plane or, it may be considered on a microscopic level such that the surface substrate atoms are important. The former view will be referred to as a "homogeneous surface" whereas the latter view will be called a "microscopic surface." Superscripts, h and m, are used here to denote the groups appropriate for homogeneous and microscopic surfaces, respectively.

There are 10 different factor groups associated with the 17 two-dimensional ordinary space groups. These factor groups only contain the operations of the identity, proper rotations around an axis perpendicular to the surface, and mirror planes perpendicular to the translational symmetry plane. Point symmetry elements appropriate for the surface substrate atoms are then limited to E, C_n, and σ_v. A particular adsite may, however, have less symmetry than the substrate factor group. If a microscopic view of the surface is taken so that the specific geometry of the surface substrate atoms is important then the adsite symmetry will be $G=C_n$ or $G=C_{nv}$. For a homogeneous surface, the adsite symmetry is $G=C_{\infty v}$. The rotation operations in G are type P whereas the mirror operations are type P*.

C. Image Molecules

Once the local site symmetry, S, has been determined for the adsorbed molecule, the group S must be correlated to the group, $\bar{S}$, describing the symmetry of the real-plus-image molecule system. The group $\bar{S}$ is defined as

$$\bar{S} = S \otimes \{E + R\}$$

where R is a combined operation of mirror reflection through the plane of the surface and charge conjugation. The operation, R, is antiunitary which makes the group $\bar{S}$ a Shubnikov Type II, or grey, point group. The grey groups do not have sets of matrices forming irreducible representations (reps); however, they do have a set of matrices obeying a more complicated set of relationships. These

sets of irreducible matrices are called irreducible corepresentations (coreps) and may be determined from the reps of S.[35] An n-dimensional rep of S with real elements correlates to an n-dimensional corep of $\bar{S}$. Complex conjugate pairs of reps of S correlate to a common two-dimensional corep of $\bar{S}$. There is, therefore, a one-to-one correlation between the vibrational modes of the adsorbed molecule and the real-plus-image molecule system. A detailed discussion of $\bar{S}$ and the correlation of S to $\bar{S}$ has been previously reported.[32]

The spectroscopic activity of surface isolated molecules is determined by the transformations of the cartesian and Raman scattering tensor (RST) components under the operations of $\bar{S}$. The general results from this analysis are that only the Z cartesian component, and the α_{XX}, α_{XY}, α_{YX}, α_{YY}, and α_{ZZ} RST components have non-zero transformations under the operations of $\bar{S}$. The axes are chosen such that Z is perpendicular to the surface. The absence of X and Y cartesian components and α_{XZ} and α_{YZ} RST components results from the cancellation of dipoles in the plane of the surface associated with the real and image molecules. Only one coordinate is necessary to describe the stretching motion of both the adsorbed molecule and its image since they are always related by the symmetry operation R, even though the nuclei undergo small displacements from equilibrium during the course of the vibration. Charge reversal of the image molecule with respect to the adsorbed molecule is responsible for the cancellation of dipole components parallel to the surface.

D. Factor Group Correlation

One last correlation between groups must be considered if the adsorbed molecules are assumed to be at a full coverage limit and adsorb in a perfect two-dimensional lattice. The real-plus-image molecule group, $\bar{S}$, must be correlated to the real-plus-image molecule factor group, $\bar{F} = F \otimes \{E + R\}$, where F is the two-dimensional factor group of the adsorbed molecules. In the homogeneous surface approximation, the space group of the adsorbed molecules can conceivably be any one of the 17 two-dimensional space groups. The particular space group is determined only by the adsorbed molecules themselves and is not dependent upon the substrate. For a microscopic surface, however, the space group of the adsorbed molecules is further restricted to be a subgroup of the two-dimensional space group of the substrate. Factor group correlations will not be considered further.

III. Application to D_{3h} Molecules Adsorbed on Surfaces

The group theory presented in Section II will now be applied to molecules having $M = D_{3h}$ symmetry adsorbed on surfaces. This system is chosen to point out the analogy between surface isolation and matrix isolation and, in addition, the local site symmetry can be examined for different orientations. Two orientations are considered for the adsorbed molecule. The first orientation has the molecular three-fold axis perpendicular to the surface whereas the second orientation has the three-fold axis parallel to the surface. For each orientation, the surface is treated as homogeneous and also as microscopic with $G = C_{2v}$.

A. Molecule Having D_{3h} Symmetry Adsorbed with Three-fold Rotation Axis Perpendicular to the Surface

Initially, the molecule is assumed to be adsorbed on a homogeneous surface such that the molecular three-fold rotation axis is perpendicular to the surface, as shown in Fig. 1a. A system similar to this was used as an example by Miller and Decius.[33] Those authors considered an AB molecule in a D_{3h} crystal field whereas here the field has the symmetry of the AB molecule and the molecule has D_{3h} symmetry. The operations in $M = D_{3h}$ are divided into the sets,

$$M(P) = \{E, 2C_3, 3C_2\}$$

and

$$M(P^*) = \{\sigma_h, 2S_3, 3\sigma_v\}$$

corresponding to P and P* operations, respectively. The operations E, $2C_3$, σ_h, and $2S_3$ correspond to rotations about an axis perpendicular to the surface whereas the operations $3C_2$ and $3\sigma_v$ correspond to rotations about axes parallel to the surface. The operation in G corresponding to rotations about an axis perpendicular to the surface is E whereas the operation corresponding to rotations around axes parallel to the surface is E*. The local site group then has the structure

$$S_h^h = \{E\}_G \otimes \{E, 2C_3\}_M + \{E^*\}_G \otimes \{3\sigma_v\}_M$$

for the hindered rotation case and

$$S_r^h = \{E\}_G \otimes \{E,\ 2C_3,\ 3C_2\}_M + \{E^*\}_G \otimes \{3\sigma_v,\ \sigma_h,\ 2S_3\}_M$$

for the free rotation limit. It is apparent that $S_h^h \leftrightarrow C_{3v}$ and $S_r^h \leftrightarrow D_{3h}$, where $\leftrightarrow$ means "isomorphous to". The order of S_r^h is 12 and the order of S_h^h is 6 so that there are 12/6 = 2 equivalent potential minima for rotations of the molecule around an axis parallel to the surface.[33]

The spectroscopic activity of the adsorbed molecule is determined by the transformations of the cartesian and RST components under the operations of the group $\bar{S}$. Only the internal optic modes in the high barrier limit will be considered. Since the following discussion contains many references to correlations between reps of M or S and coreps of $\bar{S}$, the symbol $\Gamma(M) \rightarrow D(\bar{S})$, will be used to indicate the correlation between vibrational modes transforming according to the rep Γ of M and the corep D of $\bar{S}$.

The correlation, $M \rightarrow S_h^h \rightarrow \bar{S}_h^h \leftrightarrow \bar{C}_{3v}$, is shown in Fig. 2 for the molecule adsorbed such that its C_3 axis is perpendicular to the surface. Only those modes transforming as $A_1'(M = D_{3h}) \rightarrow \bar{A}_1(\bar{S}_h^h \leftrightarrow \bar{C}_{3v})$ and $A_2''(M = D_{3h}) \rightarrow \bar{A}_1(\bar{S}_h^h \leftrightarrow \bar{C}_{3v})$ are infrared active after adsorption on the surface. Those vibrational modes transforming as $A_1'(M = D_{3h}) \rightarrow \bar{A}_1(\bar{S}_h^h \leftrightarrow \bar{C}_{3v})$ are not infrared active for the free molecule but the loss of the horizontal plane of symmetry (σ_h) upon adsorption results in a net non-zero dipole moment derivative perpendicular to the surface (Z) for the system, molecule-plus-image.

RST's are given in Fig. 2 for $\bar{S}_h^h \leftrightarrow \bar{C}_{3v}$. Neglecting resonance Raman conditions, only the $A_2'(M = D_{3h})$ and $A_1''(M = D_{3h})$ modes are Raman inactive after adsorption. The $A_2'(M = D_{3h})$ modes formally have non-zero RST elements, $\pm(\alpha_{xy} - \alpha_{yx})$. If the incident light is at frequencies far from resonance then the approximation, $\alpha_{xy} = \alpha_{yx}$, is valid so that these tensor elements are zero. The $\bar{A}_2(\bar{S}_h^h \leftrightarrow \bar{C}_{3v})$ Raman scattering tensor appropriate for the surface adsorbed molecule is, likewise, antisymmetric and ordinarily would be approximated as being zero. At least one theory of surface enhanced Raman scattering, however, is based on a resonance Raman effect. Hexter and Albrecht[27] have suggested that the surface plasmons of the metal substrate mix with the electronic states of the adsorbed molecule, thereby providing a continuum of intermediate states for the scattering. If this explanation is correct then the $\bar{A}_2(\bar{S}_h^h \leftrightarrow \bar{C}_{3v})$ modes can be Raman active.

The same molecule is now assumed to be adsorbed on a microscopic site having $G = C_{2v}$ symmetry such that the molecular three-fold axis is perpendicular to the surface, as shown in Fig. 1a, and one of the vertical mirror planes of the molecule coincides with a mirror plane of the adsite. The P and P* operations in G are

$$G(P) = \{E, C_2\}$$

$$G(P^*) = \{\sigma_{XZ}, \sigma_{YZ}\}$$

so that the local site symmetries of the molecule after adsorption are given by the groups

$$S_h^m = \{E\}_G \otimes \{E\}_M + \{\sigma_{YZ}\}_G \otimes \{\sigma_{YZ}\}_M \leftrightarrow C_s$$

and

$$S_r^m = \{E, C_2\}_G \otimes \{E, 2C_3, 3C_2\}_M + \{2\sigma_v\}_G \otimes \{3\sigma_v, \sigma_h, 2S_3\}_M .$$

There are 24/2 = 12 equivalent potential minima. The potential minima are six-fold degenerate with respect to rotations around Z and two-fold degenerate with respect to rotations around Y.

The correlation, $M = D_{3h} \rightarrow \bar{S}_h^m \leftrightarrow \bar{C}_s$ is shown in Fig. 3. Infrared activity is found only for the $\bar{A}'(\bar{S}_h^m \leftrightarrow \bar{C}_s)$ modes. All vibrational modes are predicted to be Raman active. The $E'(M = D_{3h})$ degeneracy of the free molecule is broken upon adsorption yielding the $\bar{A}'(\bar{S}_h^m \leftrightarrow \bar{C}_s)$ and $\bar{A}''(\bar{S}_h^m \leftrightarrow \bar{C}_s)$ components. Since both of these components are Raman active, they should allow a measure of the static surface field splitting. An infrared absorption experiment would not allow observation of the $\bar{A}''(\bar{S}_h^m \leftrightarrow \bar{C}_s)$ component.

The validity of the homogeneous surface approximation as opposed to a microscopic treatment of the surface can be determined most dramatically by an infrared experiment. The presence of $E'(M = D_{3h})$ and $E''(M = D_{3h})$ components in the surface spectrum would indicate that the particular adsite symmetry is important provided, of course, that the molecule is known to be adsorbed

flat on the surface. A Raman experiment, however, could reveal all vibrational modes in both cases if the $\bar{A}_2(\bar{S}_h^h \leftrightarrow \bar{C}_{3v})$ modes are active due to resonance Raman effects.

B. Molecule Having D_{3h} Symmetry Adsorbed with Three-fold Rotation Axis Parallel to Surface

If the molecule is edge-bonded to a homogeneous surface so that the molecular three-fold rotation axis is parallel to the surface, as shown in Fig. 1b, then the local site symmetry for hindered rotation is given by

$$S_h^h = \{E\}_G \otimes \{E,\ C_2(\|Z)\}_M + \{E^*\}_G \otimes \{\sigma_h,\ \sigma(YZ)\}_M \leftrightarrow C_{2v}$$

and

$$S_r^h = \{E\}_G \otimes \{E,\ 2C_3,\ 3C_2\}_M + \{E^*\}_G \otimes \{\sigma_h,\ 3\sigma_v,\ 2S_3\}_M$$

for the free rotation limit. There are then three equivalent potential minima for rotation around X.

The spectroscopic activities will be given by the transformations of the cartesian and RST components under the operations of the group $\bar{S}_h^h \leftrightarrow \bar{C}_{2v}$. The correlation of $M = D_{3h}$ to $\bar{S}_h^h \leftrightarrow \bar{C}_{2v}$ is shown in Fig. 4. Infrared activity is associated only with the $A_1'(M = D_{3h}) \rightarrow \bar{A}_1(\bar{S}_h^h \leftrightarrow \bar{C}_{2v})$ and $E'(M = D_{3h}) \rightarrow \bar{A}_1(\bar{S}_h^h \leftrightarrow \bar{C}_{2v})$ modes.

Raman activity is associated only with $A_1'(M = D_{3h}) \rightarrow \bar{A}_1(\bar{S}_h^h \leftrightarrow \bar{C}_{2v})$, $A_1''(M = D_{3h}) \rightarrow \bar{A}_2(\bar{S}_h^h \leftrightarrow \bar{C}_{2v})$, $E'(M = D_{3h}) \rightarrow \bar{A}_1(\bar{S}_h^h \leftrightarrow \bar{C}_{2v})$, and $E''(M = D_{3h}) \rightarrow \bar{A}_2(\bar{S}_h^h \leftrightarrow \bar{C}_{2v})$ modes. The site group splitting predicted for the $E'(M = D_{3h})$ and $E''(M = D_{3h})$ modes cannot be measured since each has a spectroscopically inactive component.

If the surface is treated microscopically with $G = C_{2v}$ and the molecule is adsorbed on edge as shown in Fig. Ib with the molecular σ_h mirror plane coinciding with the σ_{YZ} mirror plane of the surface, then the groups describing the local site symmetries are

$$S_h^m = \{E\}_G \otimes \{E\}_M + \{C_2\}_G \otimes \{C_2\}_M + \{\sigma_{YZ}\}_G \otimes \{\sigma_h\}_M + \{\sigma_{XZ}\}_G \otimes \{\sigma_{XZ}\}_M \leftrightarrow C_{2v}$$

and

$$S_r^m = \{E, C_2\}_G \otimes \{E, 2C_3, 3C_2\}_M + \{2\sigma_v\}_G \otimes \{3\sigma_v, \sigma_h, 2S_3\}_M.$$

Since these groups are isomorphous to those groups appropriate for the homogeneous surface approximation, infrared and Raman experiments cannot determine the importance of the adsite symmetry.

IV. Interpretive Problems with Raman Spectra of Adsorbed Molecules

Interpreting the Raman spectrum of molecules adsorbed on metal surfaces is not only a matter of analyzing the observed spectrum in terms of the group theoretical selection rules expected for

various possible orientations of the molecules. In this section, some of the difficulties with spectral interpretation are discussed. Discriminating Raman active vibrational modes of different symmetry by the use of their polarization properties should provide a clue to the orientation of surface adsorbed molecules. For rough surfaces, however, the observed Raman scattering intensity results from scattering contributions from adsorbed molecules having a distribution of orientations relative to the laboratory axes. The observed polarization properties can differ greatly from that expected for molecules adsorbed on a flat surface. This is demonstrated in IV(A). Additional factors which can influence the observed intensities are briefly considered in IV(B).

A. Depolarization from Rough Surfaces

The vibrational modes of molecules adsorbed on rough surfaces often do not exhibit the polarization properties predicted by the RST's appropriate for a particular adsorbed molecule. The Raman spectrum of CN^- adsorbed on silver was found to be completely depolarized by Billmann et al.[2] In a study of the Raman scattering intensity of pyridine adsorbed on silver as a function of scattering angle, Pettinger and co-workers found only a small change in intensity with S-polarized light vs. P-polarized light.[15] Part of the difficulty in using polarization to discriminate between various vibrational modes is due to the possibility that the RST for a particular vibrational mode may have more non-zero elements in the laboratory coordinate system than the RST appropriate for the local site coordinate system. This is illustrated in the

following example. Electron microscopy reveals that an electrochemically roughened silver surface consists of nodules ~600 to 1000 nm in diameter.[22] This suggests that a model surface consisting of many small metal spheres might reasonably approximate the real surface. Only one of these spheres will be considered here and the substrate will be assumed to be a perfect electrical conductor. The sphere size is large relative to molecular dimensions so that the surface can be approximated as being flat in the region of an individual adsorbed molecule. The orientation of an adsorbed molecule relative to the laboratory coordinate system depends upon its position on the sphere; hence, the surface curvature is important in this respect. The homogeneous surface approximation is used and the local site symmetry of an adsorbed molecule is assumed to be $S_h^h = C_{2v}$. Except for the requirement that the molecular C_2 symmetry axis (z) is perpendicular to the surface, orientational order is neglected. Once adsorbed, the molecule is not allowed to rotate at the site. Fig. 5 shows an experimental right angle scattering geometry with light incident along Y′ and scattered along Z′. Only those molecules adsorbed on the quarter of the spherical surface between the plane defined by the X′ and Z′ axes and the plane defined by the X′ and -Y′ axes are simultaneously exposed to the incident light and can scatter along Z′. The Raman scattering tensors in the local site coordinate system for the real-plus-image molecule system are:

$$\underset{\sim}{\alpha}(\bar{A}_1) = \begin{bmatrix} \alpha_{XX} & 0 & 0 \\ 0 & \alpha_{YY} & 0 \\ 0 & 0 & \alpha_{ZZ} \end{bmatrix} ; \quad \underset{\sim}{\alpha}(\bar{A}_2) = \begin{bmatrix} 0 & \alpha_{XY} & 0 \\ \alpha_{YX} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} ;$$

$$\underset{\sim}{\alpha}(\bar{B}_1) = \underset{\sim}{\alpha}(\bar{B}_2) = 0$$

Only those vibrational modes transforming as the coreps $\bar{A}_1(\bar{S}_h^h \leftrightarrow \bar{C}_{2v})$ or $\bar{A}_2(\bar{S}_h^h \leftrightarrow \bar{C}_{2v})$ are predicted to be Raman active. The RST's in the laboratory coordinate system, $\underset{\sim}{\alpha}'$, are given by

$$\underset{\sim}{\alpha}' = \underset{\sim}{A}\ \underset{\sim}{\alpha}\ \underset{\sim}{A}^{-1}$$

where the matrix $\underset{\sim}{A}$ is

$$\begin{bmatrix} \cos\xi\cos\theta + \sin\xi & \sin\phi\sin\theta & \cos\xi\sin\theta - \sin\xi\sin\phi\cos\theta & -\sin\xi\cos\phi \\ -\cos\phi\sin\theta & & \cos\phi\cos\theta & -\sin\phi \\ \sin\xi\cos\theta - \cos\xi & \sin\phi\sin\theta & \sin\xi\sin\theta + \cos\xi\sin\phi\cos\theta & \cos\xi\cos\phi \end{bmatrix}$$

ϕ is the angle between the ZY plane and the X´Y´ plane, ξ is the angle between the ZX´ plane and the Z´X´ plane, and θ is the angle of rotation around the local site axis Z. The angles are defined in this way to facilitate averaging over the allowed molecular orientations. Four polarization experiments are possible with this scattering geometry, these being Y´(X´X´)Z´, Y´(X´Y´)Z´, Y´(Z´X´)Z´, and Y´(Z´Y´)Z´. A molecule adsorbed at some point on the experimentally accessible quadrant of the sphere will, in general,

have all non-zero RST elements in the laboratory coordinate system. Raman scattering will then be expected for both $\bar{A}_1(\bar{S}_h^h \leftrightarrow \bar{C}_{2v})$ and $\bar{A}_2(\bar{S}_h^h \leftrightarrow \bar{C}_{2v})$ symmetry modes in each of the four scattering experiments. Raman scattering will arise from many adsorbed molecules, each having a different RST, hence, the intensity will be proportional to the squares of the appropriate RST elements in the laboratory coordinate system integrated over the angles $0 \leq \phi \leq \pi/2$, $0 \leq \xi \leq \pi$, and $0 \leq \theta \leq 2\pi$. The elements of $\underset{\approx}{\alpha}(\bar{A}_1)$ have contributions from each of the diagonal elements of $\underset{\approx}{\alpha}(\bar{A}_1)$. Without knowing the relative magnitudes of α_{XX}, α_{YY}, and α_{ZZ}, it is impossible to compare the relative intensities expected for the four polarized Raman experiments; for the $\bar{A}_2(\bar{S}_h^h \leftrightarrow \bar{C}_{2v})$ modes, however, the RST elements in the laboratory coordinate system may each be expressed in terms of α_{XY}, thus allowing a comparison of intensities. The averages are $\langle \alpha^2_{X'X'} \rangle = 0.34\alpha^2_{XY}$, $\langle \alpha^2_{X'Y'} \rangle = 0.15\alpha^2_{XY}$, $\langle \alpha^2_{Z'X'} \rangle = 0.18\alpha^2_{XY}$, and $\langle \alpha^2_{Z'Y'} \rangle = 0.25\alpha^2_{XY}$. The greatest deviation is only by a factor of about 2, with the S and P polarizations having the most intensity. When other factors are also considered, such as multilayer coverages, partial long range ordering, and other substrate geometries, it is not surprising that very little information can be obtained from depolarization measurements.

B. Additional Factors Contributing to Observed Raman Spectrum

There are several additional factors which can make the observed Raman spectrum of surface adsorbed molecules differ from that predicted by the transformations of the RST components under the

operations of the group $\bar{S}$. The number of molecules adsorbed on a surface is so small ($\sim 10^{15}$ molecules cm^{-2}) that the vibrational modes must exhibit SERS in order to be observed. SERS may not be found for all Raman active vibrational modes; hence, an erroneous conclusion about molecular orientation may simply result from a lack of sufficient Raman intensity. Another factor which can make it difficult to determine the orientation of surface adsorbed molecules is that the group $\bar{S}$ is appropriate only for perfect electrical conductors in which the image molecule is identical to the adsorbed molecule except for charge conjugation. If the substrate cannot be approximated as a perfect electrical conductor then those vibrational modes having non-zero XZ and YZ RST components under the group S will retain some residual Raman activity. Multilayer coverages can cause still another problem when trying to elucidate the orientation of adsorbed molecules by Raman spectroscopy. If those molecules in the outer layers do not have the same orientation as do those in direct contact with the surface, then their local site symmetries and, therefore, the Raman activity will be different for molecules in outer layers as opposed to the first monolayer. Some vibrational modes which are inactive for those molecules in direct contact with the surface may be active in the outer layers and will contribute to the total Raman spectrum.

V. Application to Real Systems

Although many studies of molecules adsorbed on metal surfaces have been reported, very few can be used as definitive tests for the validity of spectroscopic selection rules. An attempt is made in this section to apply the selection rules presented here to the systems, pyridine/silver and ethylene/silver. For both systems, the surface is approximated as a homogeneous two-dimensional plane and the substrate as a perfect electrical conductor. The adsorbed molecule is not allowed to rotate at the site and will be treated as being surface isolated.

A. Application to Pyridine

Two orientations are considered for pyridine adsorbed on a metal surface. The first is that the molecule is bonded "perpendicular" to the surface as shown in Fig. 6a whereas the second orientation, shown in Fig. 6b has the molecule adsorbed horizontal to the surface.

The P and P* operations of $M = C_{2v}$ are

$$M(P) = \{E, C_2\}$$
$$M(P^*) = \{\sigma_{xz}, \sigma_{yz}\}$$

so that the effective surface site symmetry for the adsorbed molecule shown in Fig. 6a is

$$S_h^h = \{E\}_G \otimes \{E, C_2\}_M + \{E^*\}_G \otimes \{\sigma_{xz}, \sigma_{yz}\}_M \leftrightarrow C_{2v}.$$

Fig. 7 shows the correlation, $M = C_{2v} \rightarrow S_h^h \rightarrow \bar{S}_h^h \leftrightarrow \bar{C}_{2v}$. Since the cartesian axes (x, y, z) of the molecule coincide with the cartesian axes (X, Y, Z) of the surface, a change of coordinates is not required to relate molecular parameters to surface parameters. Only the $A_1(M = C_{2v}) \rightarrow \bar{A}_1(\bar{S}_h^h \leftrightarrow \bar{C}_{2v})$ modes have infrared activity and only the $A_1(M = C_{2v}) \rightarrow \bar{A}_1(\bar{S}_h^h \leftrightarrow \bar{C}_{2v})$ and $A_2(M = C_{2v}) \rightarrow \bar{A}_2(\bar{S}_h^h \leftrightarrow \bar{C}_{2v})$ modes have Raman activity after adsorption. The free molecule has $10A_1 + 3A_2 + 9B_1 + 5B_2$ fundamental vibrational modes, all of which are Raman active with only 24 being infrared active. The adsorbed molecule should have 13 Raman active and 10 infrared active internal optic mode fundamentals.

The structure of the local site group for the adsorbed molecule shown in Fig. 6b is

$$S_h^h = \{E\}_G \otimes \{E\}_M + \{E^*\}_G \otimes \{\sigma_{xz}\}_M \leftrightarrow C_s.$$

Fig. 8 shows the correlation, $M = C_{2v} \rightarrow S_h^h \rightarrow \bar{S}_h^h \leftrightarrow \bar{C}_s$. The molecular axes (x, y, z) are related to the surface axes (X, Y, Z) by:

$$\begin{vmatrix} x \\ y \\ z \end{vmatrix} = \begin{vmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{vmatrix} \begin{vmatrix} X \\ Y \\ Z \end{vmatrix}$$

As seen in Fig. 8, all vibrational modes of the adsorbed molecule shown in Fig. 6b are Raman active whereas only the $\bar{A}'(\bar{S}_h^h \leftrightarrow \bar{C}_s)$ modes are infrared active.

There have been several Raman investigations of liquid and solution pyridine establishing the symmetries of various vibrational modes. The out-of-plane modes, $A_2(M = C_{2v})$ and $B_2(M = C_{2v})$, were reported by Kakiuti and co-workers in a force constant analysis in which pyridine and its deuterium analogs were used.[36] Berezin and co-workers[37] and Green and co-workers[38] have reported $A_1(M = C_{2v})$ and $B_1(M = C_{2v})$ frequencies. A comprehensive assignment of the vibrational modes of pyridine was recently reported by DiLella and Stidham.[39]

Numerous Raman investigations of pyridine adsorbed on Ag electrodes have been reported. Creighton et al.[14] found several Raman bands in the 200 - 4000 cm^{-1} spectral region. A mode at 669 cm^{-1} was attributed to a $B_1(M = C_{2v})$ ring deformation while the remaining modes were assigned as being $A_1(M = C_{2v})$ motions. Bands at 1008 and 1036 cm^{-1} result from pyridine bonded perpendicular to the Ag surface, according to Fleischmann et al.[1] Hexter and Albrecht reported several modes of $B_1(M = C_{2v})$ and $B_2(M = C_{2v})$ symmetry in addition to the $A_1(M = C_{2v})$ modes.[27] No modes of $A_2(M = C_{2v})$ symmetry were observed. The $B_1(M = C_{2v})$ and $B_2(M = C_{2v})$ modes have the same frequencies after adsorption as the liquid so that there is some uncertainty as to whether they are due to surface adsorbed pyridine or bulk liquid pyridine. According to Albrecht[40], the $A_2(M = C_{2v})$, $B_1(M = C_{2v})$, and $B_2(M = C_{2v})$ modes are observable for adsorbed pyridine only after extensive roughening of the Ag electrode by numerous oxidation-reduction cycles. The $A_1(M = C_{2v})$ modes, however, require but little preliminary surface preparation. Smardzewski and co-workers[8]

recently reported Raman scattering data for pyridine adsorbed on silver under ultrahigh vacuum conditions. They observed only the totally symmetric $A_1(M = C_{2v})$ modes. Frequency shifts of as much as 15 cm^{-1} relative to solution studies were found.

The observation of the symmetric, $A_1(M = C_{2v})$, modes alone does not allow the orientation of adsorbed pyridine to be elucidated. Those studies which report scattering from vibrational modes selected from each of the symmetry species of M also make it difficult to determine the orientation of the adsorbed molecules. Scattering from all modes could result from orientational disorder in outer adsorbed layers, the adsite symmetry could lower the local site symmetry below that expected in the homogeneous surface approximation, or there could be a breakdown in the approximation that the substrate is a perfect electrical conductor.

Pyridine adsorbed on silver is not a good system to determine if the spectroscopic selection rules predicted by the correlation, $M \rightarrow S \rightarrow \bar{S}$, are valid. The pyridine molecule has C_{2v} symmetry which is advantageous in the sense that all vibrational modes of bulk pyridine are Raman active and the cartesian components belong to separate one-dimensional reps. The point group is, therefore, non-trivial yet not overly complex. The disadvantage is that the intense Raman active modes of bulk pyridine all have $A_1(M = C_{2v})$ symmetry. The absence of vibrational modes of different symmetry in the Raman spectrum of the adsorbed molecule is not conclusive that they are not Raman active. Many of these modes could exhibit SERS by several orders of magnitude and still not be observed in the surface Raman spectrum.

B. Application to Ethylene

Pearce and Sheppard have studied ethylene adsorbed on the silica-supported metals Pt, Pd, Ni, and Rh.[31] The metal surface selection rules used in this work and by Nichols and Hexter[32] are based on ideas proposed by those authors to explain their observations. Their results support a model in which both carbon atoms are bonded to the surface, as shown in Fig. 9. SERS spectra of ethylene adsorbed on silver have been recorded by Moskovits and DiLella.[16] Their conclusions are that the molecule is lying on the surface.

In addition to those vibrational modes which are normally Raman active in the gas phase, Moskovits and DiLella observed several new modes which they assigned to ν_4, ν_7, ν_{10}, and ν_{11} which are of symmetry species $A_u(M = D_{2h})$, $B_{1u}(M = D_{2h})$, $B_{2u}(M - D_{2h})$, and $B_{3u}(M = D_{2h})$, respectively.[16] If these assignments are correct, then the local site symmetry of the adsorbed molecule must be reduced to C_2, C_s, or C_1 provided the selection rules used here are valid. One way in which the local site symmetry can be reduced is to treat the surface microscopically. The group G must then be one of the groups C_n or C_{nv} (n = 1, 2, 3, 4, 6), thereby allowing S_h^m to have lower symmetry than S_h^h. Another possibility to consider is that monolayer coverages were not used. The outer layers may not have the same orientation as does the layer immediately adjacent to the surface so that more modes may become Raman active. If the surface cannot be approximated as a perfect electrical conductor, then a local site symmetry as high as C_{2v} will still allow all vibrational modes to become Raman active.

VI. Discussion

A procedure for determining the allowed surface site symmetries, S, has been presented as an extension of that proposed by Miller and Decius[33] for matrix isolation in crystals. An analogy can be drawn between the perturbing field experienced by a molecule matrix isolated in a three-dimensional crystal and that experienced by a molecule adsorbed on a surface. In the former case, the field has the symmetry of the host lattice site whereas in the latter case, the field has the symmetry of the adsite. If the surface is viewed as a homogeneous two-dimensional plane, then the symmetry of the adsite is described by the group $G = C_{\infty v}$. If the surface cannot be viewed as an unstructured homogeneous plane so that the perturbing field experienced by the adsorbed molecule must be considered on a microscopic level, then the adsite will be described by the group appropriate for the substrate atoms. This can only be one of the groups $G = C_n$ or $G = C_{nv}$.

The symmetry operations of the local site symmetry group, S, consist of an operation in M applied to the molecule combined with an operation in G applied to the substrate. A mapping of the operations in M and G to their corresponding operations in their isomorphous Longuett-Higgins groups allows the operations to be identified as permutation, P, or permutation-inversion, P*, operations. The Longuet-Higgins groups are based on the invariance of the hamiltonian with respect to permutations of

identical nuclei and inversion of the positions of all particles through the center of mass, hence, if a P* operation is applied to either the molecule of the substrate, a P* operation must alse be applied to the other. This restricts the operations in S to be combinations of P operations in M with P operations in G and combinations of P* operations in M with P* operations in G.

The local site symmetry of the adsorbed molecule is, in general different for the homogeneous surface approximation as opposed to the microscopic surface approximation. The group S_h^m may be of lower symmetry than S_h^h so that more vibrational modes may become active if the symmetry of the surface substrate atoms is important. Knowledge of the microscopic site symmetry and the magnitude of the $S_h^h \rightarrow S_h^m$ correlation splitting should provide a probe to determine the effect of a particular adsite on the molecule-surface interaction. Usually, however, the orientation of the molecule is not known and some confusion could result from a similarity between a group S_h^m appropriate for a high symmetry orientation and a group S_h^h appropriate for a low symmetry orientation.

An additional factor to consider is that for some particular adsorbed molecule orientation, the internal optic modes may be described by S_h^h whereas the external optic modes may be described by S_h^m. The external optic modes involve motions of the whole molecule with respect to the surface and the particular molecule-surface bond is, therefore, important. The frequencies of internal optic modes, however, are primarily a property of the molecule

and the presence of a surface is of secondary importance. The correlation splitting resulting from $M \rightarrow S_h^h$ should be much greater than that resulting from $S_h^h \rightarrow S_h^m$ for the internal optic modes of the adsorbed molecule.

Discrimination of vibrational modes of even monolayer coverages of adsorbed molecules by polarized Raman experiments may be difficult. The RST's in the laboratory coordinate system for molecules adsorbed on rough surfaces will, in general, have all non-zero elements for all Raman active symmetry species.

Finally, one difficulty in determining surface orientation from the observed spectra is that multilayer coverages are usually used. Molecules in the outer layers may not have the same orientation as do those molecules in direct contact with the surface, yet, they still contribute to the observed Raman spectrum.

Figure Captions

Figure 1. a) Molecule having D_{3h} symmetry adsorbed on a surface such that the C_3 axis is perpendicular to the surface, b) same molecule adsorbed with the C_3 axis parallel to the surface.

Figure 2. Correlation diagram for the molecule shown in Fig. 2a. The surface is homogeneous.

Figure 3. Correlation diagram for the molecule shown in Fig. 2a. The surface is microscopic with G = C_{2v}.

Figure 4. Correlation diagram for the molecule shown in Fig. 2b. The surface is homogeneous or microscopic with G = C_{2v}.

Figure 5. Experimental right angle scattering geometry for molecules adsorbed on a small sphere. The molecular axes are x, y, z, the surface axes are X, Y, Z, and the laboratory axes are X', Y', Z'.

Figure 6. Adsorbtion geometries of surface adsorbed pyridine. a) The C_2 axis of pyridine is perpendicular to the surface, b) The molecule is adsorbed flat on the surface.

Figure 7. Correlation diagram for pyridine adsorbed on a homogeneous surface as shown in Fig. 7a.

Figure 8. Correlation diagram for pyridine adsorbed on a homogeneous surface as shown in Fig. 7b.

Figure 9. Proposed geometry of surface adsorbed ethylene.

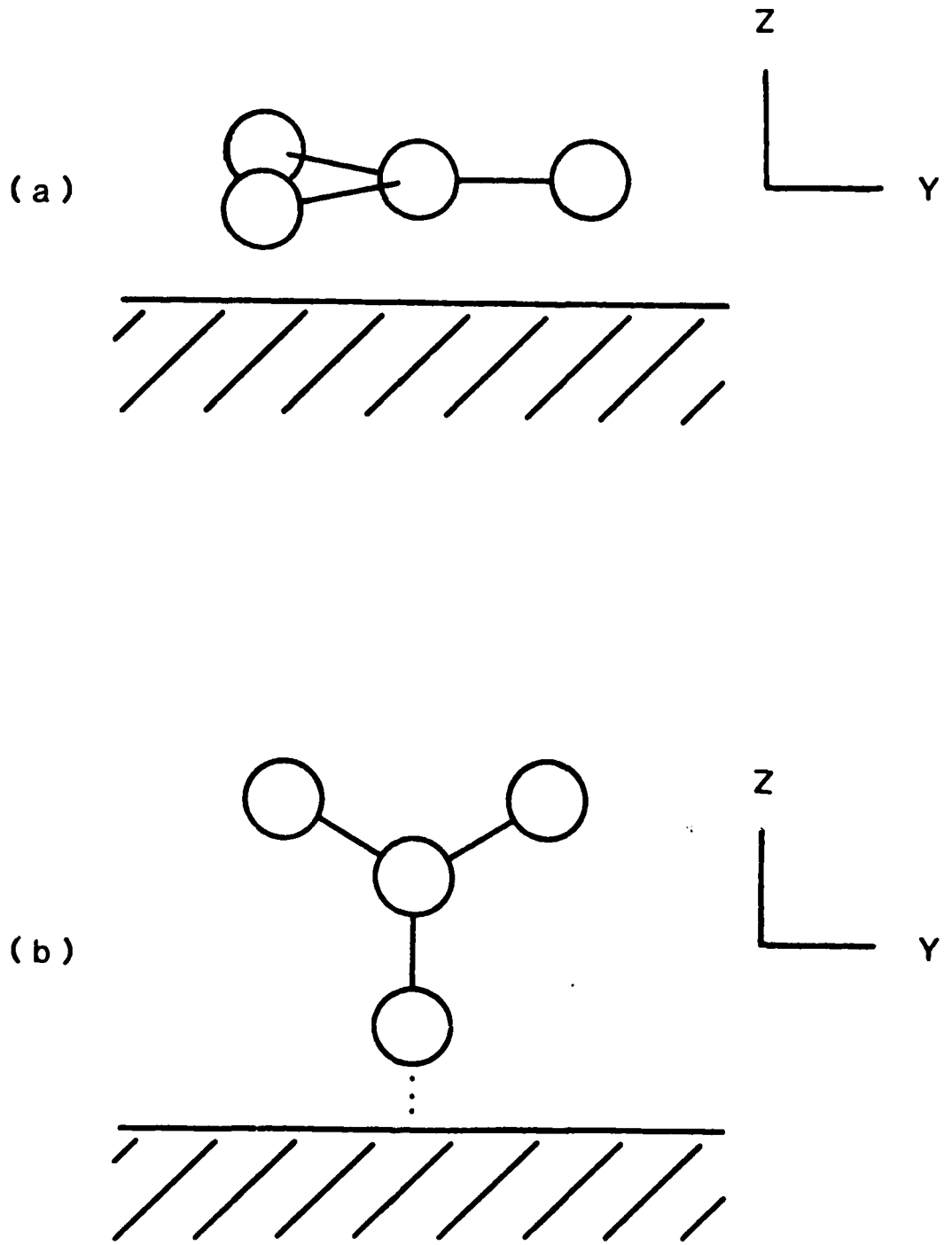


Fig. 1

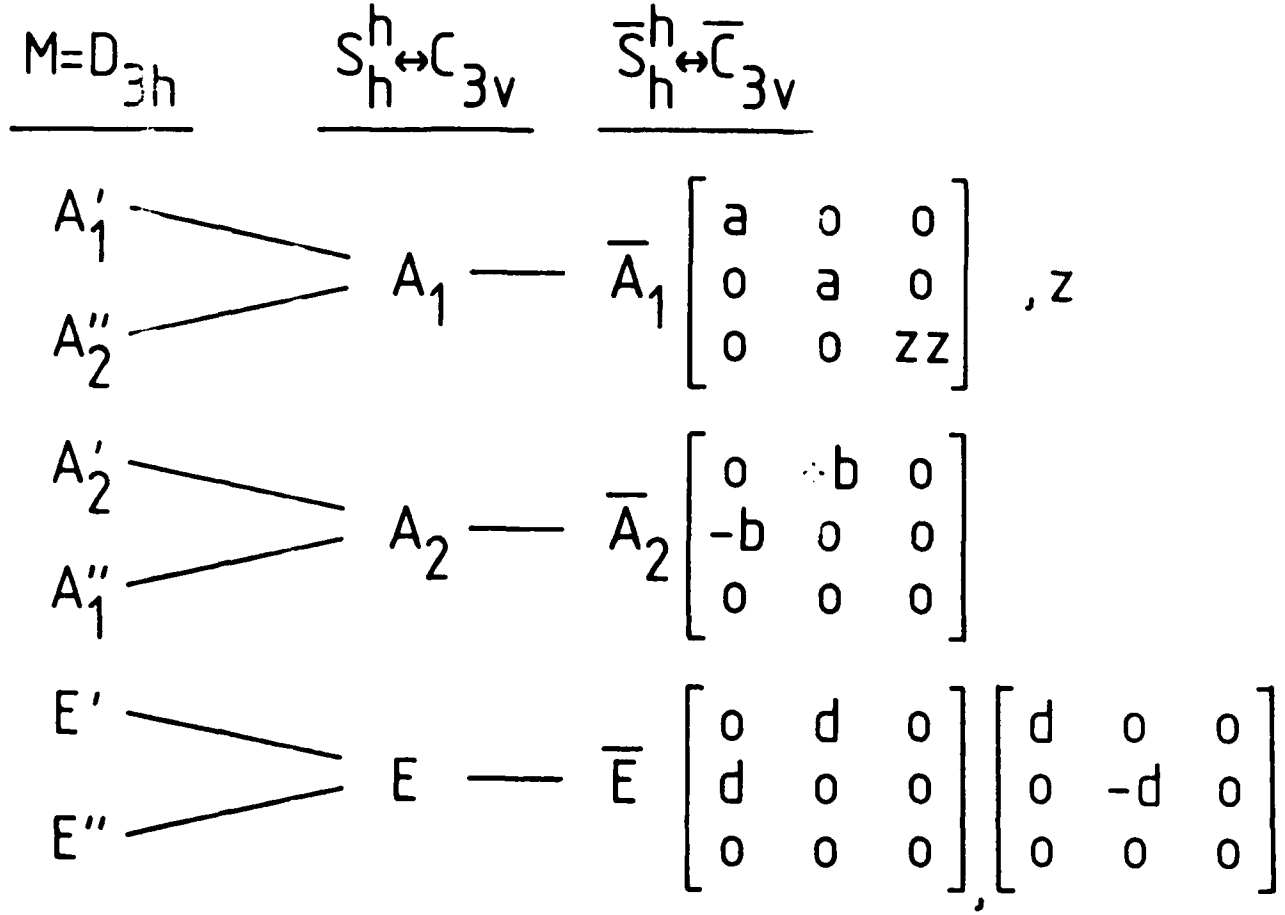
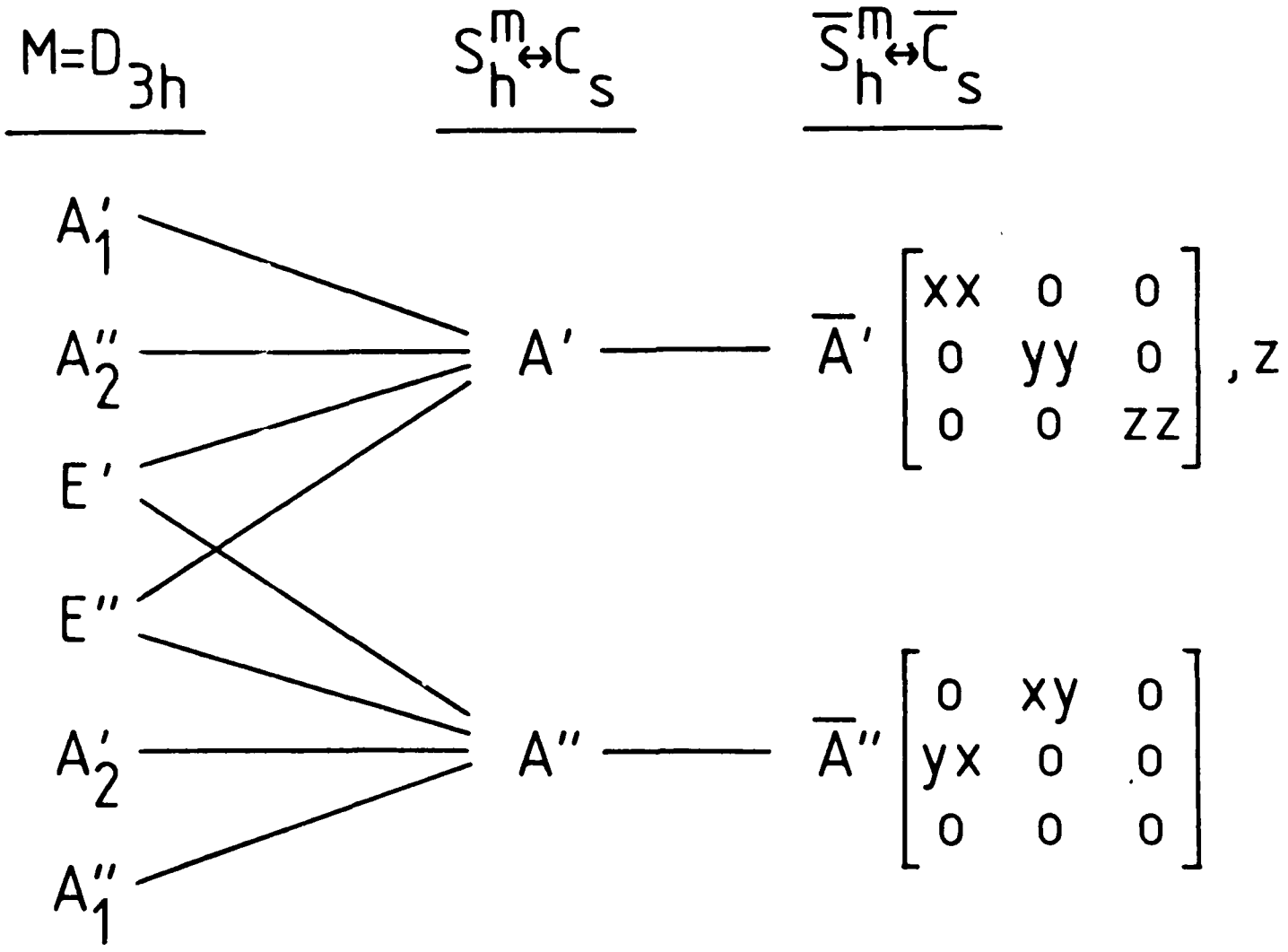

M=D3h
S^h_h↔C3v
S̄^h_h↔C̄3v
A1'
A2''
A1
Ā1
a 0 0
0 a 0
0 0 zz
, z
A2'
A1''
A2
Ā2
0 -b 0
-b 0 0
0 0 0
E'
E''
E
Ē
0 d 0
d 0 0
0 0 0
d 0 0
0 -d 0
0 0 0
a=(xx+yy)/2 ; b=(xy-yx)/2 ; d=(xx-yy)/2

Fig. 2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Sh m↔Cs
S̄h m↔C̄s
A1'
A2''
E'
E''
A2'
A1''
A'
A''
Ā'
Ā''
xx 0 0
0 yy 0
0 0 zz
, z
0 xy 0
yx 0 0
0 0 0

Fig. 3

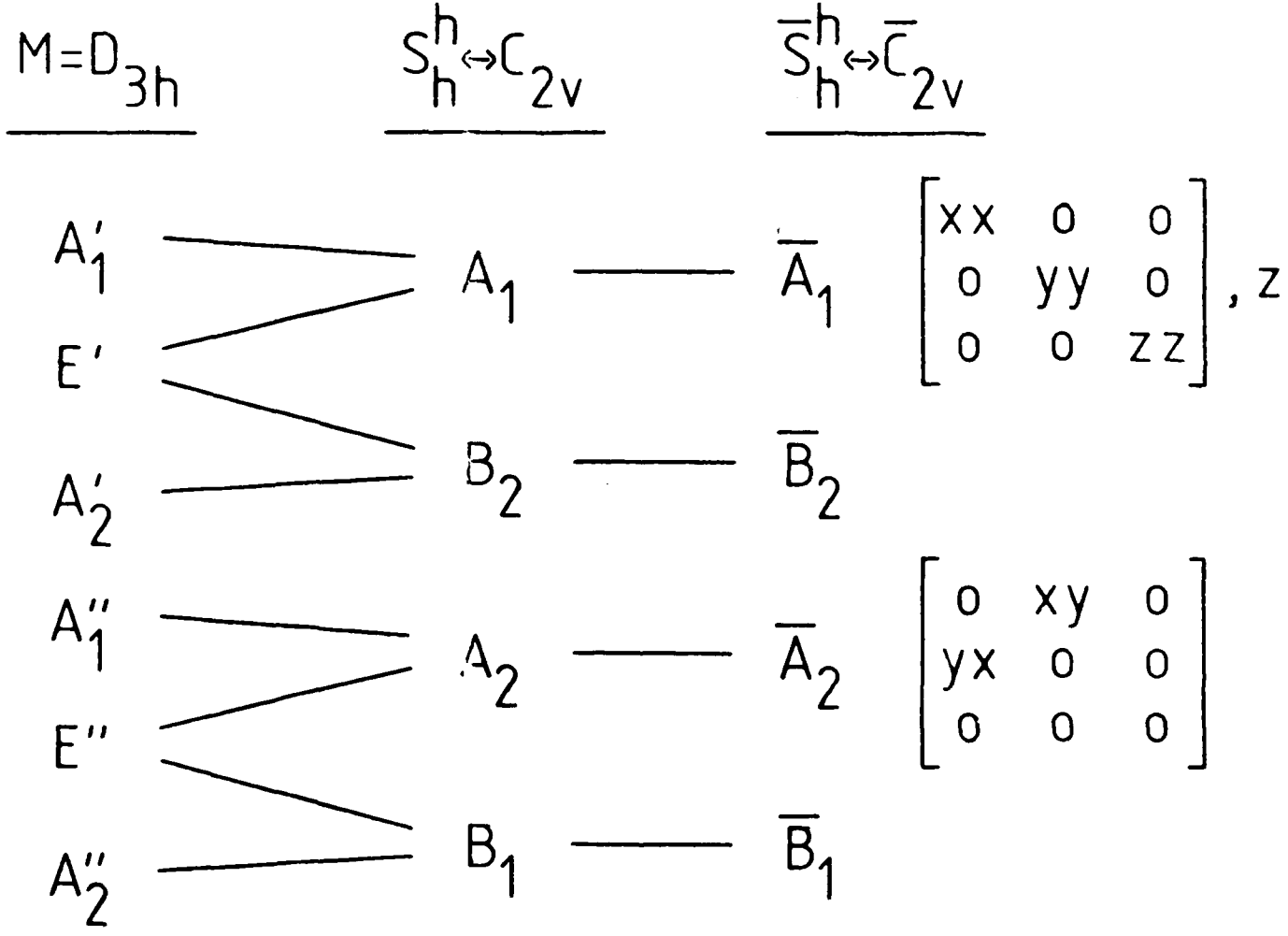

M=D3h
S_h^h↔C2v
S̄_h^h↔C̄2v
A1'
E'
A2'
A1''
E''
A2''
A1
B2
B1
A2
Ā1
B̄2
B̄1
Ā2
xx 0 0
0 yy 0
0 0 zz
, z
0 xy 0
yx 0 0
0 0 0

Fig. 4

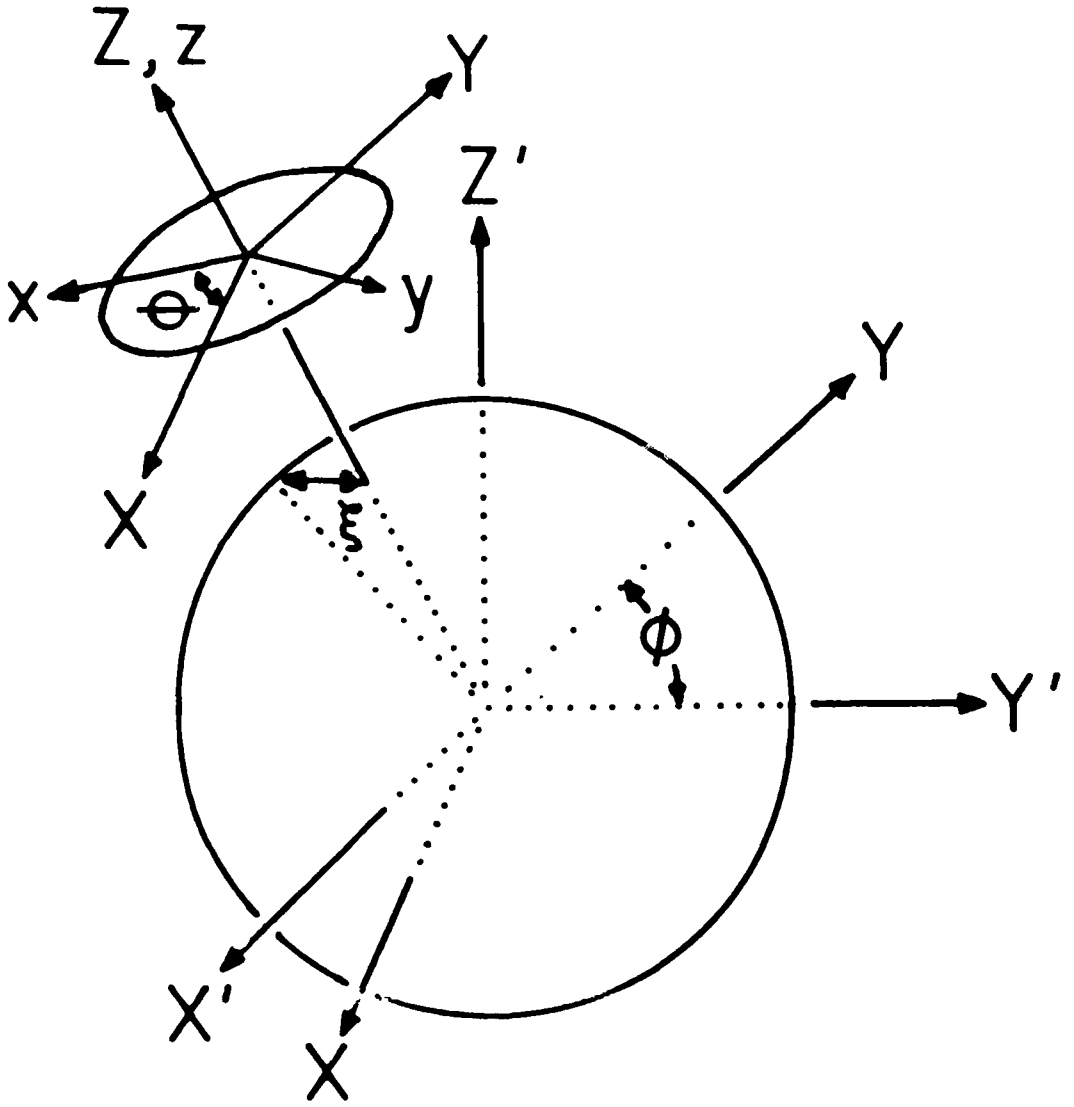
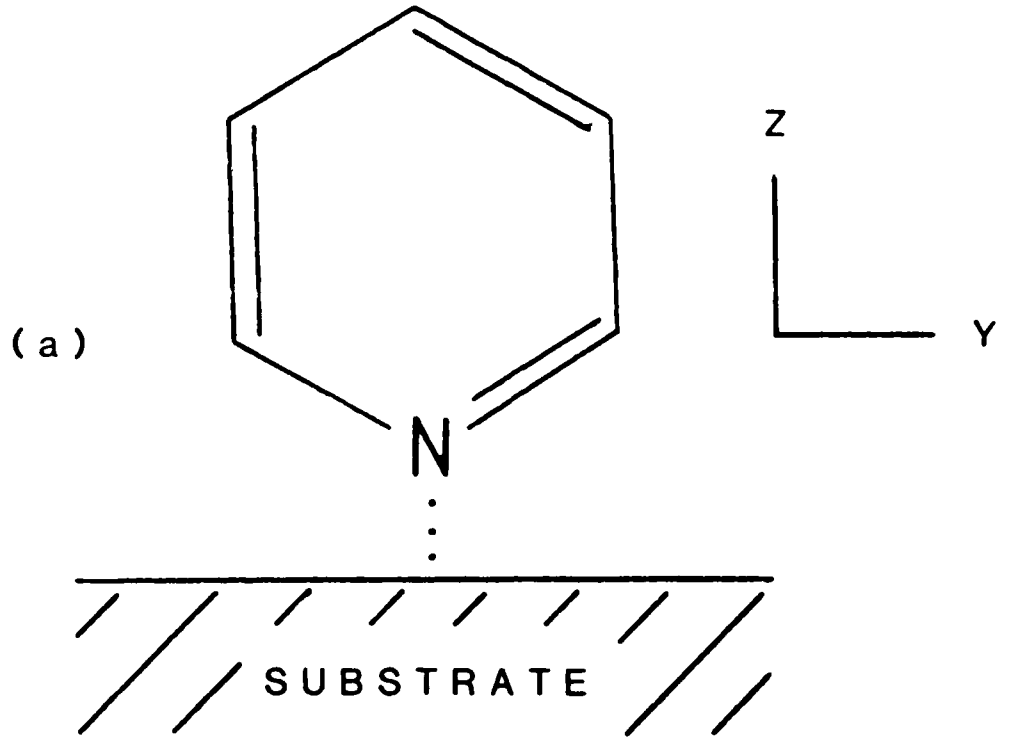


Fig. 5



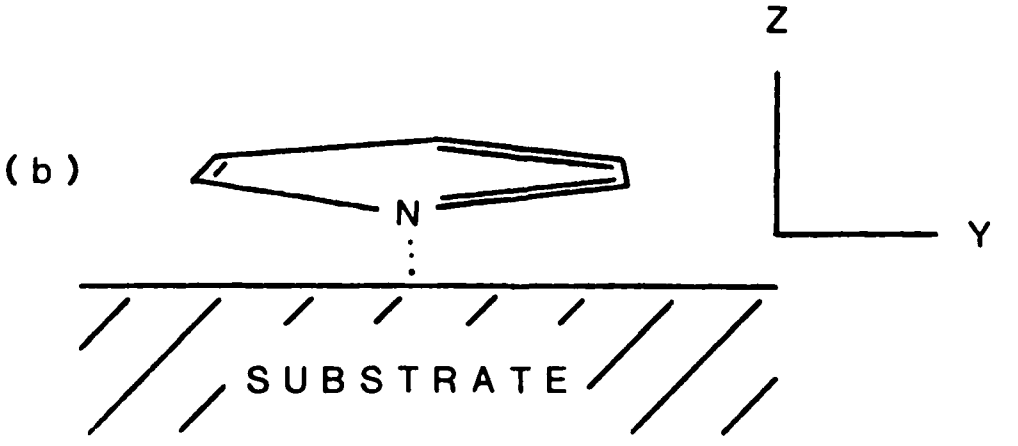


Fig. 6

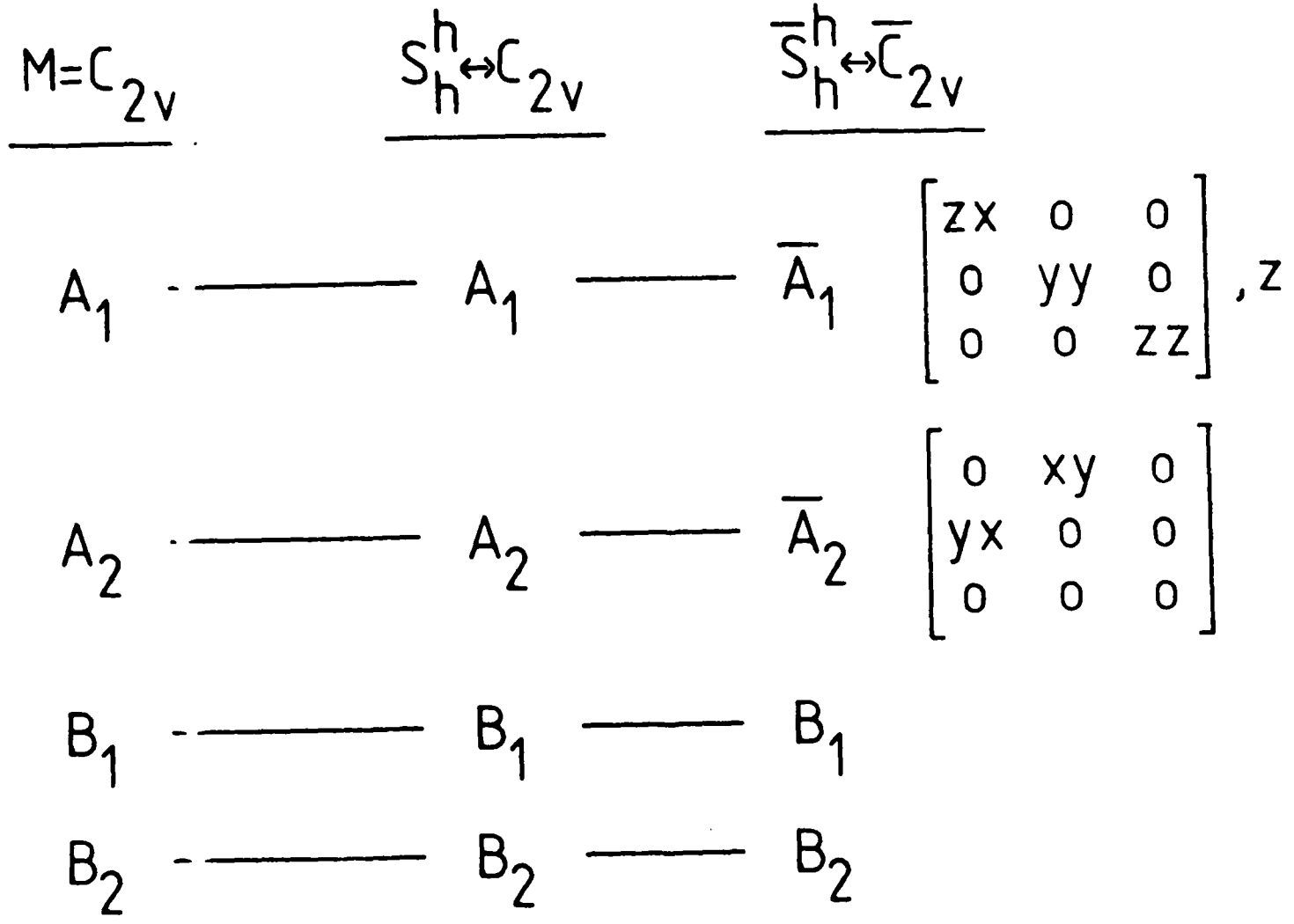

M=C2v
S_h^h↔C2v
S̄_h^h↔C̄2v
A1
A1
Ā1
zx 0 0
0 yy 0
0 0 zz
, z
A2
A2
Ā2
0 xy 0
yx 0 0
0 0 0
B1
B1
B1
B2
B2
B2

Fig. 7

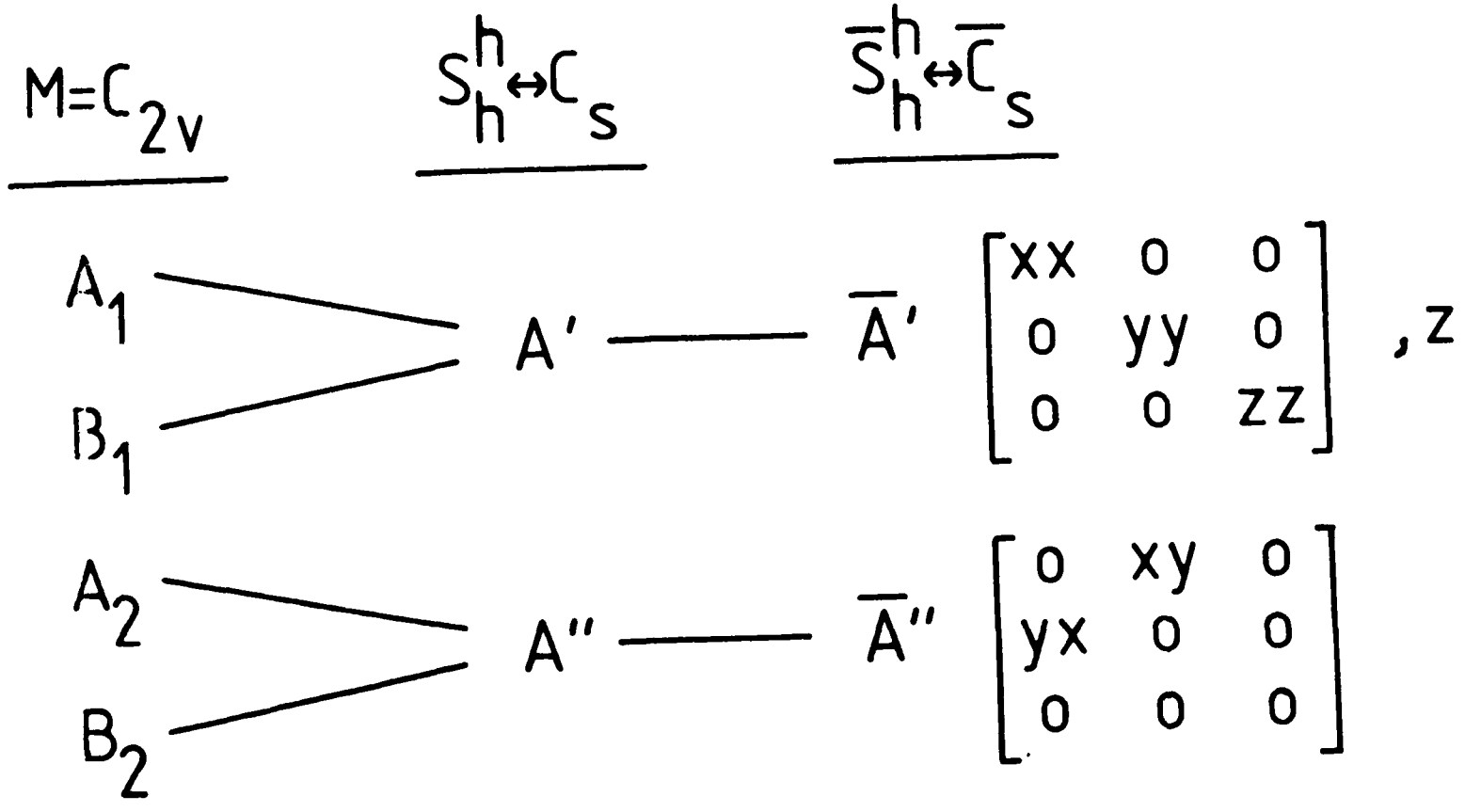


Fig. 8

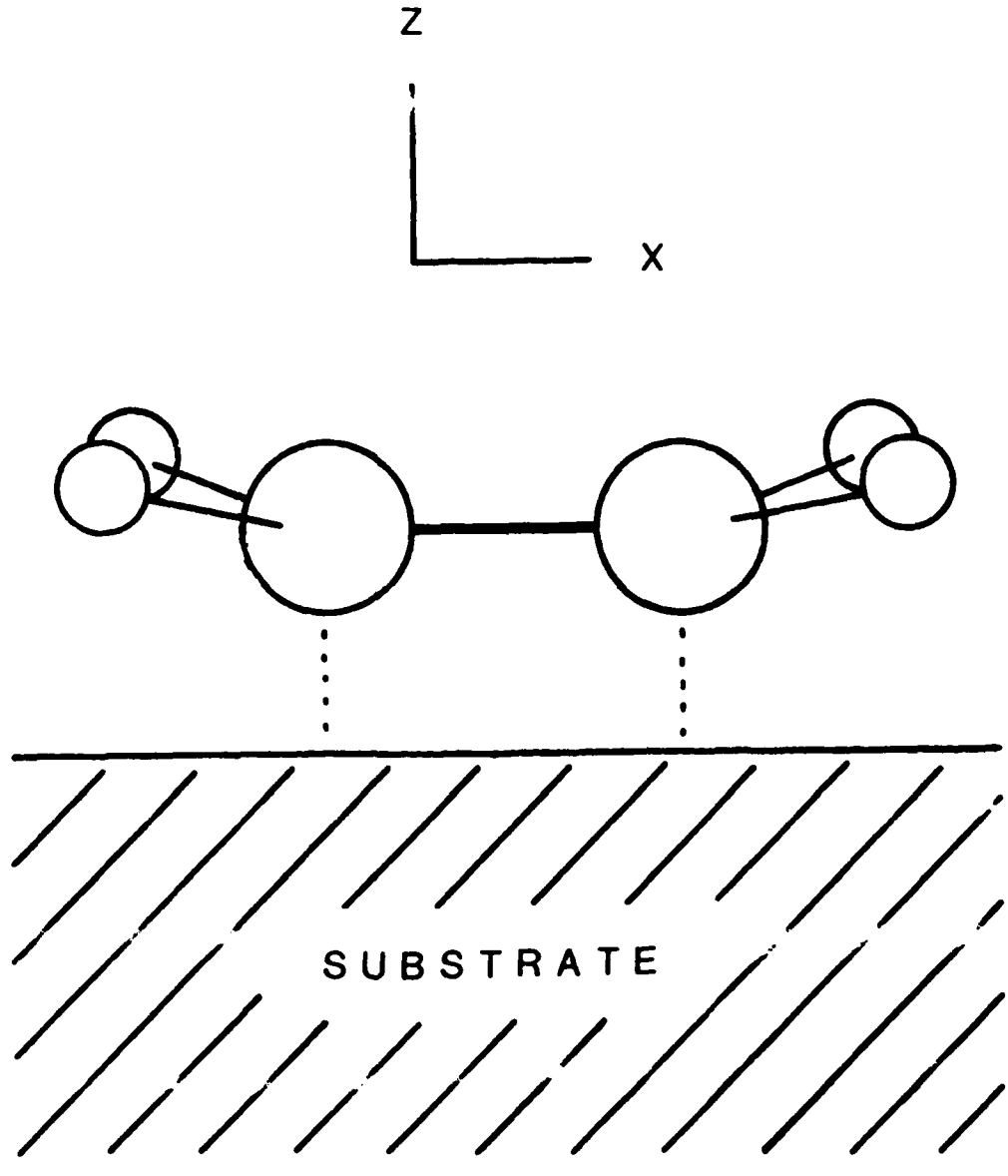


Fig. 9

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